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(54) **Method of making siloxane compositions.**

(57)   A method of making a dispersion of a high viscosity siloxane in a volatile, especially cyclic siloxane, comprises first dispersing organopolysiloxanes having at least 2 Si-OR groups, wherein R is H or alkyl in a volatile siloxane, and adding a catalyst which is either a phosphonitrile halide having the general formula $[X(PX_2=N)_nPX_3]^+[MX_{(v+1)}R_t]^-$, or a heterogeneous catalyst, selected from Li, Mg, Ca, Sr or Ba hydroxide, Na or K borate or phosphate, Rb or Cs carbonate, or carboxylates of Rb or Cs, wherein M is an element having an electronegativity of from 1.0 to 2.0, R is alkyl, X is halide, $\underline{n}$ is 1 to 6, $\underline{v}$ is the valence of M and $\underline{t}$ is from 0 to ($\underline{v}$-1).

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This invention relates to a method of making siloxane compositions, more specifically compositions wherein high viscosity polysiloxanes are dispersed in volatile, especially cyclic polysiloxanes.
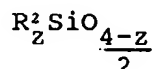
Dispersions of high viscosity polysiloxanes in cyclic polysiloxanes have been known for some time and have been commercially available. These dispersions have a variety of useful characteristics and are important ingredients in many cosmetic compositions. They are generally prepared by physically mixing high viscosity siloxanes into a medium of cyclic siloxanes which have a low viscosity. This method is tedious and requires a lot of energy to ensure a more or less homogeneous dispersion as the high viscosity materials may have a viscosity which amounts to several m^2/s. It is possible to dissolve the high viscosity materials in a solvent prior to the dispersion in the cyclic siloxanes in order to reduce the handling viscosity and hence ease the dispersion. However, this leaves the manufacturer with the added disadvantage that a solvent is present and needs to be removed. This disadvantage is all the more serious since the cyclic siloxane materials are volatile to some extent and could be at least partially removed when the solvent is removed.

There is a need for a better method of making a dispersion of high viscosity siloxanes in volatile, especially cyclic siloxanes.

We have now found a method of making such dispersion by selectively condensing hydrolisable siloxanes in the presence of volatile, especially cyclic siloxanes using specified catalysts.

According to the invention there is provided a method of making a dispersion of a high viscosity siloxane in a volatile, especially cyclic siloxane, which comprises making a first dispersion of organopolysiloxanes having at least 2 silicon-bonded groups -OR, wherein R denotes a hydrogen atom or an alkyl group having up to 6 carbon atoms in volatile siloxanes, especially cyclic siloxanes of the general formula $(R'_2SiO)_p$, wherein R' denotes hydrogen or an alkyl, alkenyl or aryl group having up to 8 carbon atoms, $\underline{p}$ denotes an integer with a value of from 3 to 12, followed by contacting said first dispersion with a catalyst which is either (A) a phosphonitrile halide having the general formula $[X(PX_2=N)_nPX_3]^+[MX_{(v-t+1)}R_t]^-$, or (B) a heterogeneous catalyst, selected from lithium hydroxide, magnesium hydroxide, calcium hydroxide, strontium hydroxide, barium hydroxide, sodium borate, sodium phosphate, potassium borate, potassium phosphate, rubidium carbonate, caesium carbonate and carboxylates of rubidium and caesium of the general formula Q.CO.OZ, wherein M is an element having an electronegativity of from 1.0 to 2.0 according to Pauling's scale, Q represents an alkyl group having from 1 to 6 carbon atoms or an alkenyl group having from 2 to 5 carbon atoms, R is an alkyl group having up to 12 carbon atoms, X denotes a halide atom, Z represents Rb or Cs, $\underline{n}$ has a value of from 1 to 6, $\underline{v}$ is the valence or oxidation state of M and $\underline{t}$ has a value of from 0 to ($\underline{v}$-1).

Organopolysiloxanes which are suitable for the making of the first dispersion are well known and commercially available materials. They have units of the general formula

$$R_z^2 SiO_{\frac{4-z}{2}}$$

wherein R^2 denotes a monovalent hydrocarbon atom having up to 8 carbon atoms and z has a value of from 0 to 3. R^2 may be an alkyl, aryl, aralkyl or alkaryl group. It is, however, preferred that 80% of all R^2 groups are lower alkyl groups or aryl groups, most preferably methyl groups. Most preferably substantially all R^2 groups are methyl groups. It is also preferred that the value of $\underline{z}$ is 2 for the majority of units, making the organopolysiloxane a polydiorganosiloxane which is a substantially linear polymer. Preferred polymers may have small amounts of units wherein the value of $\underline{z}$ is 0 or 1, but such units should not amount to more than 5% of the total number of units in the organopolysiloxane. Units where $\underline{z}$ equals 3 are end-blocking units and no more than 2 of these units will be present unless some branching in the organopolysiloxane has occurred. The organopolysiloxanes must have at least 2 silicon-bonded groups -OR, wherein R denotes a hydrogen atom or an alkyl group having up to 6 carbon atoms. It is preferred that each terminal silicon atom of the organopoly-siloxane has one such silicon-bonded group -OR. Preferred organopolysiloxanes accordingly have the general formula $RO[SiR_2^2O]_mR$, wherein R and R^2 are as defined above, and m is an integer with a value of at least 2. Most preferably R is hydrogen. A suitable example is dimethylsilanol endblocked polydimethylsiloxane. The organopolysiloxanes which are useful for making the first dispersion are preferably linear siloxanes with a viscosity of from 20 to 10,000mm^2/s. However, in order to facilitate the mixing process it is preferred to use polymers of slightly lower viscosity, e.g. 20 to 1000mm^2/s, more preferably 50 to 500mm^2/s and most preferably 60 to 200mm^2/s.

Volatile siloxanes are well known and commercially available materials. They are siloxane polymers which are either short chain or cyclic siloxanes, having a viscosity at room temperature of no more than 10mm^2/s, and a boiling point under atmospheric pressure of no more than 250°C. Preferred volatile siloxanes are dis-

iloxanes, e.g. hexamethyldisiloxanes. Most preferred are cyclic siloxanes, or mixtures including cyclic siloxanes. It is important that the volatile siloxanes do not have any silicon-bonded groups -OR as defined above, to avoid the polymerisation reaction by condensation of the volatile siloxanes with the organopolysiloxanes having silicon-bonded -OR groups.

Cyclic siloxanes which are useful are also well known and commercially available materials. They have the general formula $(R'_2SiO)_p$, wherein R' denotes hydrogen or an alkyl, alkenyl or aryl group having up to 8 carbon atoms, p denotes an integer with a value of from 3 to 12. Preferably at least 80% of all R' groups are methyl of phenyl groups, most preferably methyl. It is most preferred that substantially all R' groups are methyl groups. Preferably the value of p is from 3 to 6, most preferably 4 or 5. Examples of suitable cyclic siloxanes are octamethyl cyclotetrasiloxane, decamethyl pentacyclosiloxane, cyclopenta (methylvinyl) siloxane, cyclotetra (phenylmethyl) siloxane and cyclopenta methylhydrosiloxane. One particularly suitable commercially available material is a mixture of octamethylcyclo-tetrasiloxane and decamethylcyclopentasiloxane.

The first dispersion may be made in any convenient way, preferably by mixing the ingredients mechanically. Standard equipment can be used for this dispersion. Suitable equipment includes ribbon blending, homogenisers etc. The ratio of organopolysiloxanes to volatile or cyclic siloxanes in the first dispersion may vary from 1/100 to 10/1. It is, however, preferred that the ratio is from 1/100 to 1/1, more preferably from 1/20 to 1/2, most preferably 1/10 to 1/4. Higher amounts of volatile siloxanes are particularly preferred, as this allows for the final dispersion to have a viscosity which can easily be handled, even when the high viscosity siloxane has a viscosity of several m^2/s.

Organopolysiloxanes which are used in the formation of the first dispersion may also include endblocking units. These are e.g. organosilicon compounds which have only one silicon-bonded group -OR per molecule, and may be silanes (e.g. trimethylsilanol, vinyldimethylsilanol) or siloxanes (e.g. α-hydroxydimethylsiloxane).

Suitable catalysts for the method of the invention may be any of a number of materials.

Catalysts (A) which are useful in the method of the invention have a cationic phosphonitrile part and an anionic part which has been derived from a Lewis acid. The cationic phosphonitrile part is a linear oligomeric or polymeric phosphonitrile halide having the general formula $[X(PX_2=N)_nPX_3]^+$ wherein n denotes an integer having a value of from 1 to 6. It is preferred that the halogen X is a chlorine atom. Phosphonitrile halide cationic parts with a value for n which is higher than 6 are less suitable as catalysts. Most preferred are the cationic phosphonitrile halide parts in which the value of n is from 2 to 4. It is particularly preferred that the amount of phosphonitrile halide polymer in which n has a value of 2 is as high as possible as this gives the most active catalyst. Particularly preferred is a catalyst which exclusively consists of compounds according to the above formula in which the value of n is 2.

The anionic part of the catalyst (A) is derived from a Lewis acid and has the formula $[MX_{(v-t+1)}R_t]^-$. Although it is preferred that the value of t is zero alkyl groups may be included. Preferably the Lewis acid based anion contains a halide X which is the same as the halide of the phosphonitrile cationic part, i.e. most preferably a chlorine. The element M of the Lewis acid part is an electropositive element having an electronegativity value according to Pauling's scale of from 1 to 2, preferably from 1.2 to 1.9, most preferably 1.5 to 1.9. Suitable elements are found in Groups Ib, IIa, IIb, IIIa, IVa, IVb, Va, Vb, VIb, VIIb and VIII of the Periodic Table. They include Al, B, Be, Mg, Sb and Si . It is preferred that the difference in electronegative value between the phosphorus atom of the phosphonitrile part of the catalyst and the M element is as large as possible within the preferred range, giving improved catalytic activity when this value is larger. A suitable compound is the one where the Lewis acid derived portion is based on antimony, especially $SbCl_3$ or $SbCl_5$ or aluminium, especially $AlCl_3$. An example of such suitable catalyst (A) has the formula
$[Cl_3P=N-(PCl_2=N)_s-PCl_3]^+[SbCl_6]^-$, wherein s has a value from 1 to 4.

Phosphonitrile halide catalysts (A) which are useful in the method of the invention have been described fully in our copending application No. G.B. 9103656.6 and may be made by reacting in the presence of an aromatic hydrocarbon or of a chlorinated aliphatic or aromatic hydrocarbon, e.g. toluene, sym-tetrachloroethane or 1,2,4-trichlorobenzene, as inert solvent, a phosphorus pentahalide, e.g. phosphorus pentachloride, an ammonium halide, e.g. ammonium chloride and a selected Lewis acid. The reaction may be carried out at a temperature between 100 and 220°C, followed by separating the reaction products from the solids and the volatile components, thus isolating the liquid reaction product. The reagents may be contacted for a period of time which may vary from 2 to 10 hours. It is preferred to continue the reaction for a period in excess of 6 hours. From 0.1 to 1 mole, preferably 0.3 to 0.6 mole of the selected Lewis acid is provided for each mole of phosphorus pentahalide. The catalyst which is useful in the method of the invention can be conveniently stored in solvent, e.g. CH_2Cl_2 preferably under a blanket of nitrogen.

The phosphonitrile halide catalysts (A) may be used at a concentration of from 1 to 500ppm by weight based on the total weight of the organopolysiloxanes which are to be polymerised. Preferably from 5 to 150ppm by weight are used, most preferably from 5 to 50ppm. The amount of catalyst used in the method of the invention

may be reduced when the temperature at which the organosilicon compounds and the catalyst are contacted is increased. The method of the invention may conveniently be carried out at room temperature. The temperature may also be as high as 150°C. Preferably, however, the temperature range is from 10 to 100°C, most preferably from 20 to 50°C. The higher the temperature the more chance that some of the volatile, especially cyclic siloxanes are lost from the reaction mixture due to their lower boiling point. If higher temperatures are used it is preferred to increase the pressure of the reaction to some extent. Catalysts (A) can easily be neutralised at the end of the polymerisation reaction in order to stabilise the reaction product, e.g. in respect of its viscosity. The neutralisation may be done at any stage of the condensation process, e.g. as soon as the desired viscosity of the organopolysiloxanes is reached. Neutralisation agents for the catalysts are alkaline materials, preferably lightly alkaline materials for example primary, secondary and tertiary amines, ammonia, amides, imides and cyclic diamines. Examples of suitable neutralisation agents are diethylamine, propylamine, ammonia, hexamethyldisilazane, piperazine, methylmorpholine and succinamide.

Due to the low amount of catalyst (A) required and the ease of terminating the condensation reaction, Catalyst (A) is particularly useful in both batch and continuous processes. Catalyst (A), though also useful as a rearrangement catalyst for polydiorganosiloxanes, is much more effective as a condensation catalyst. It is, therefore, particularly interesting to use Catalyst (A) in the method of the invention as rearrangement would only occur when the condensation reaction has finished.

A second group of useful catalysts in the method of the invention is concerned with a group of heterogeneous catalysts (B). Because of their heterogeneous nature these catalysts are also particularly adapted for use in processes involving manufacture on a continuous, rather than a batch, basis. Properly employed such so-called "continuous processes" avoid the delays and costs common to batch processing, for example those involved in the charging and discharging of the reaction vessel and separation of the catalyst material from the product. When carrying out the process of this invention in a continuous mode contact between the catalyst material and the organosilicon compound may be achieved by passing the organosilicon compound over or through a bed of the catalyst material. When employing more viscous reactants or products it may be necessary to adjust the porosity of the bed by granulation of the catalyst or other means. We have found that a particularly suitable form of bed for continuous operation can be obtained by depositing the catalyst substance in or on an inert particulate material, for example silica, having a particle size appropriate to the desired porosity of the bed.

A first type of heterogeneous catalyst (B) consists of borates or phosphates of sodium or potassium. Specific examples of such catalysts are $K_2B_4O_7.4H_2O$, $K_2BO_2.xH_2O$, $K_2B_{10}O_{16}.8H_2O$, $K_3PO_4.xH_2O$, $Na_2B_4O_7.4H_2O$, $NaBO_3.4H_2O$, $NaBO_2.xH_2O$ and $Na_3PO_4.12H_2O$. The sodium and potassium compounds may be employed in their anhydrous or hydrated forms. In the case of the phosphate compounds the phosphate anion should not contain hydrogen. Thus, the phosphates of sodium and potassium employed according to this invention do not include the hydrogen phosphates.

A second type of heterogeneous catalyst (B) is any hydroxide of lithium, magnesium, calcium, strontium or barium, the preferred substances being strontium hydroxide and barium hydroxide. The compounds may be employed in their anhydrous or hydrated forms.

A third type of heterogeneous catalyst (B) is a carbonate or carboxylate of rubidium or caesium. In the general formula of the carboxylates Q may be for example methyl, ethyl, propyl, hexyl, vinyl or allyl. Specific examples of catalyst (B) are rubidium carbonate, caesium carbonate, rubidium acetate, caesium propionate, caesium butyrate and rubidium acrylate.

The particle size of the heterogeneous catalyst (B) is not critical. Generally, the smaller the particles the greater the catalytic surface available. However, very fine particle size powders may be more difficult to remove from the condensation product.

In one of its aspects the process of this invention involves contacting the first dispersion with the heterogeneous catalyst (B) at a temperature at which the desired rate of molecular weight increase occurs. The temperatures employed may vary within wide limits for example from about 30°C to about 200°C. Reaction at the lower temperatures is, however, normally too slow for commercial purposes and the process is preferably carried out at temperatures within the range from about 70°C to 150°C. It is also preferred to accelerate the removal of water formed during the condensation reaction by carrying out the process under reduced pressure, that is, at a pressure less than normal atmospheric and most preferably less than about 0.5 bar. One method of carrying out the process is by means of a batch procedure. For example, the catalyst (B) may be codispersed in the first dispersion and this mixture raised to the required temperature. Alternatively, the first dispersion may be preheated prior to the addition of the catalyst (B). Advantageously the mixture is agitated during the reaction period to maintain the catalyst in suspension. Sufficient catalyst (B) is employed to achieve the desired rate of condensation having regard to the nature and geometry of the processing equipment, temperature and other factors. From considerations of speed of reaction and economy of operation we prefer to employ from about

0.001 to about 8% by weight more preferably 0.1 to 5% of the catalyst (B) based on the weight of the organopolysiloxane in the first dispersion.

Termination of the condensation reaction when using catalyst (B) in the method of the invention may be achieved by lowering the temperature of the mixture, and/or raising the reaction pressure to atmospheric and/or by separation or neutralisation of the catalyst.

The final product obtained by the method of the invention is a dispersion of a high viscosity siloxane, having a structure which is dependant on the structure of the organopolysiloxane starting materials used in making the first dispersion. When the preferred organopolysiloxanes are used the final high viscosity siloxanes have the average formula $RO[SiR^2_2O]_mSiR^2_2OR$, wherein R and R^2 are as defined above and $\underline{m}$ has a value which is substantially higher than the number of organosiloxane units present in the organopolysiloxanes used to make the first dispersion. The viscosity of the high viscosity siloxanes may be as low as 10,000mm²/s or as high as several millions of mm²/s, thus forming a siloxane gum. The final product will have a weight ratio of high viscosity siloxane polymer to cyclic siloxane which is very close to the ratio of organopolysiloxane to cyclic siloxanes of the first dispersion. This is due to the fact that the only change in weight is due to the formation and removal of H_2O molecules or ROH molecules upon condensation or the organopolysiloxanes. Traces of catalyst which may remain in the final dispersion may be removed by known methods, i.e. filtration, evaporation etc.

There now follow a number of examples which illustrate the invention. All parts, ratios and percentages are by weight unless otherwise stated.

Example 1

0.12 mole of PCl_5, 0.08 mole of NH_4Cl and 0.04 mole of $SbCl_5$ were allowed to react together in 60ml of symtetrachloroethane at its refluxing temperature of 147°C for 3.5 hours. After the reaction the solution was filtered to remove insoluble compounds, followed by removal of the solvent under reduced pressure. A bright yellow liquid was obtained which slowly crystallised upon cooling. The resulting catalyst was analysed by NMR (nuclear magnetic resonance) spectroscopy. It was found to be a 50/50 mixture of $[PCl_3=N-PCl_2=N-PCl_3]^+$-$[SbCl_6]^-$ and $[PCl_3=N-(PCl_2=N)_2-PCl_3]^+[SbCl_6]^-$ while no $[PCl_6]^-$ anion was observed. 50 parts of dimethylsilanol endblocked polydimethylsiloxane were mixed with 50 parts of octamethyltetracyclosiloxane and homogenised into a first dispersion. 48ppm based on the weight of the polydimethylsiloxane of the catalyst as prepared above were added and the mixture allowed to react at 20°C under reduced pressure of 20mm Hg. After 15 minutes the reaction was halted by neutralising the catalyst with 50 ppm of diethylamine. The finished dispersion consisted of 50 parts of a high viscosity siloxane having a viscosity of at least 500,000mm²/s and thus forming a siloxane gum in 50 parts of unchanged octamethyl cyclotetrasiloxane, giving the dispersion an overall viscosity of 12,000mm²/s.

Example 2

13 parts of an α,w-hydroxyl dimethylpolysiloxane having an average structure of $H[OSi(CH_3)_2]_nOH$, wherein $\underline{n}$ has the average value of 32, were mixed with 83 parts of a mixture of octamethylcyclotetrasiloxane and decamethylpentacyclosiloxane. The mixture was heated to reflux temperature (about 180°C) at atmospheric pressure in the presence of 2% of anhydrous potassium carbonate, based on the weight of the dimethylpolysiloxane. Condensation water was collected in a Dean & Stark apparatus. After 7 hours the reaction was stopped. The catalyst was filtered out and the final product was analysed by gel permeation chromatography. This analysis showed that the polydimethylsiloxane had condensed to form high viscosity siloxanes with an average molecular weight of 196,464, and that the cyclic siloxanes were unreacted. The final product was a clear dispersion of the high viscosity siloxanes in the cyclic siloxanes.

Example 3

15 parts of an α,w-hydroxyl dimethylpolysiloxane having an average structure of $H[OSi(CH_3)_2]_nOH$, wherein $\underline{n}$ has the average value of 34, were mixed with 85 parts of a mixture of octamethylcyclotetrasiloxane and decamethylpentacyclosiloxane. The mixture was heated to reflux temperature (about 180°C) at atmospheric pressure in the presence of 0.7% of barium hydroxide octahydrate, based on the weight of the dimethylpolysiloxane. Condensation water was collected in a Dean & Stark apparatus. After 45 minutes the reaction was stopped. The catalyst was filtered out and the final product was analysed by gel permeation chromatography. This analysis showed that the polydimethylsiloxane had condensed to form high viscosity siloxanes with an average molecular weight of 245,000 and that the cyclic siloxanes were unreacted. The final product was a clear dis-

persion of the high viscosity siloxanes in the cyclic siloxanes.

Example 4

5   50 parts of an α,w-hydroxyl dimethylpolysiloxane having an average structure of $H[OSi(CH_3)_2]_nOH$, wherein n has the average value of 34, were mixed with 50 parts of a mixture of octamethylcyclotetrasiloxane and decamethylpentacyclosiloxane. The mixture was heated to reflux temperature (about 200°C) at atmospheric pressure in the presence of 5% of strontium hydroxide octahydrate, based on the weight of the dimethylpolysi-loxane. Condensation water was collected in a Dean & Stark apparatus. After 2 hours the reaction was stopped.
10   The catalyst was filtered out and the final product was analysed by gel permeation chromatography. This analysis showed that the polydimethylsiloxane had condensed to form high viscosity siloxanes with an average molecular weight of 170,258 and that the cyclic siloxanes were unreacted. The final product was a clear dispersion of the high viscosity siloxanes in the cyclic siloxanes.

15   Example 5

15 parts of an α,w-hydroxyl dimethylpolysiloxane having an average structure of $H[OSi(CH_3)_2]_nOH$, wherein n has the average value of 34, were mixed with 85 parts of a mixture of octamethylcyclotetrasiloxane and decamethylpentacyclosiloxane. The mixture was heated to reflux temperature (about 130°C) at 260 mm Hg
20   pressure in the presence of 5% of rubidium carbonate, based on the weight of the dimethylpolysiloxane. Con-densation water was collected in a Dean & Stark apparatus. After 8 hours the reaction was stopped. The catalyst was filtered out and the final product was analysed by gel permeation chromatography. This analysis showed that the polydimethylsiloxane had condensed to form high viscosity siloxanes with an average molecular weight of 283,796 and that the cyclic siloxanes were unreacted. The final product was a clear dispersion of the high
25   viscosity siloxanes in the cyclic siloxanes.

Example 6

15 parts of an α,w-hydroxyl dimethylpolysiloxane having an average structure of $H[OSi(CH_3)_2]_nOH$, wherein
30   n has the average value of 34, were mixed with 85 parts of a mixture of octamethylcyclotetrasiloxane and decamethylpentacyclosiloxane. The mixture was heated to reflux temperature (about 180°C) at atmospheric pressure in the presence of 5% of tri-sodium orthophosphate dodecahydrate, based on the weight of the dimethylpolysiloxane. Condensation water was collected in a Dean & Stark apparatus. After 8 hours the reac-tion was stopped. The catalyst was filtered out and the final product was analysed by gel permeation
35   chromatography. This analysis showed that the polydimethylsiloxane had condensed to form high viscosity siloxanes with an average molecular weight of 266,390 and that the cyclic siloxanes were unreacted. The final product was a clear dispersion of the high viscosity siloxanes in the cyclic siloxanes.

Example 7

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50 parts of an α,w-hydroxyl dimethylpolysiloxane having an average structure of $H[OSi(CH_3)_2]_nOH$, wherein n has the average value of 34, were mixed with 50 parts of a mixture of octamethylcyclotetrasiloxane and decamethylpentacyclosiloxane. The mixture was heated to reflux temperature (about 100°C) at 75mm Hg pressure in the presence of 5% of sodium metaborate octahydrate, based on the weight of the dimethylpolysi-
45   loxane. Condensation water was collected in a Dean & Stark apparatus. After 8 hours the reaction was stopped. The catalyst was filtered out and the final product was analysed by gel permeation chromatography. This analysis showed that the polydimethylsiloxane had condensed to form high viscosity siloxanes with an average molecular weight of 266,390 and that the cyclic siloxanes were unreacted. The final product was a clear dis-persion of the high viscosity siloxanes in the cyclic siloxanes.

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Examples 8 - 11

x parts of an α,w-hydroxyl dimethylpolysiloxane having an average structure of $H[OSi(CH_3)_2]_nOH$, wherein n has the average value of 34, were mixed with y parts of a mixture of octamethylcyclotetrasiloxane and
55   decamethylpentacyclosiloxane. The mixture was heated to reflux temperature (about 130°C) at 300mm Hg pressure in the presence of 5% of lithium hydroxide monohydrate, based on the weight of the dimethylpolysi-loxane. Condensation water was collected in a Dean & Stark apparatus. After 2 hours the reaction was stopped. The catalyst was filtered out and the final product was analysed by gel permeation chromatography. This

analysis showed that the polydimethylsiloxane had condensed to form high viscosity siloxanes with an average molecular weight of z and that the cyclic siloxanes were unreacted. The final product was a clear dispersion of the high viscosity siloxanes in the cyclic siloxanes. The values of $\underline{x}$, $\underline{y}$ and $\underline{z}$ are given in the table below.

Example	x	y	z
8	15	85	80,000
9	35	65	145,000
10	50	50	245,000
11	75	25	349,000

Claims

1. A method of making a dispersion of a high viscosity siloxane in a volatile siloxane, which comprises making a first dispersion of organopolysiloxanes having at least 2 silicon-bonded groups -OR, wherein R denotes a hydrogen atom or an alkyl group having up to 6 carbon atoms in a volatile siloxane, followed by contacting said first dispersion with a catalyst which is either (A) a phosphonitrile halide having the general formula $[X(PX_2=N)_nPX_3]^+[MX_{(v-t+1)}R_t]^-$, or (B) a heterogeneous catalyst, selected from lithium hydroxide, magnesium hydroxide, calcium hydroxide, strontium hydroxide, barium hydroxide, sodium borate, sodium phosphate, potassium borate, potassium phosphate, rubidium carbonate, caesium carbonate and carboxylates of rubidium or caesium of the general formula $Q.CO.OZ$, wherein M is an element having an electronegativity of from 1.0 to 2.0 according to Pauling's scale, Q represents an alkyl group having from 1 to 6 carbon atoms or an alkenyl group having from 2 to 5 carbon atoms, R is an alkyl group having up to 12 carbon atoms, X denotes a halide atom, Z represents Cs or Rb, $\underline{n}$ has a value of from 1 to 6, $\underline{v}$ is the valence or oxidation state of M and $\underline{t}$ has a value of from 0 to $(\underline{v}\text{-}1)$.

2. A method according to Claim 1, wherein the volatile siloxane is a cyclic siloxane of the general formula $(R'_2SiO)_p$ wherein R' denotes hydrogen or an alkyl, alkenyl or aryl group having up to 8 carbon atoms, $\underline{p}$ is an integer with a value of from 3 to 12.

3. A method according to Claim 1 or 2, wherein substantially all groups R' and R^2 are methyl groups.

4. A method according to any one of the preceding claims, wherein the organopolysiloxane is a substantially linear siloxane polymer, having on each terminal siloxane unit a silicon-bonded group OH.

5. A method according to any one of the preceding claims, wherein the viscosity of the organopolysiloxane used is from 50 to 500mm²/s.

6. A method according to any one of the preceding claims, wherein the weight ratio of organopolysiloxane to volatile siloxane used in the first dispersion is from 1/20 to 1/2.

7. A method according to any one of the preceding claims, wherein the catalyst is neutralised when the high viscosity siloxane has reached the desired viscosity.

8. A method according to any one of the preceding claims, wherein catalyst (A) is used in an amount of from 5 to 50ppm by weight based on the weight of the organopolysiloxane.

9. A method according to any one of the preceding claims wherein M denotes Sb and $\underline{n}$ has a value of 2.

10. A method according to any one of Claims 1 to 7, wherein catalyst (B) is used in the form of a catalyst bed in an amount of from 0.1-5% by weight based on the weight of the organopolysiloxane.

European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP   92 30 1836

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
P,A	FR-A-2 663 941 (DOW CORNING) * claim 1; example 1 * ---	1-10	C08G77/08
A	EP-A-0 305 737 (WACKER) * example 1 * ---	1-10	
A	EP-A-0 208 285 (WACKER) * claim 1; example 1 * ---	1-10	
A	EP-A-0 382 366 (DOW CORNING) * claims 1-3 * ---	1-10	
A	EP-A-0 382 367 (DOW CORNING) * claim 1; example 1 * ---	1-10	
A	EP-A-0 206 525 (DOW CORNING) * example 1 * -----	1-10	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5) C08G C08J

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	02 JULY 1992	LENTZ J.C.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
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T : theory or principle underlying the invention
E : earlier patent document, but published on, or
    after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding
    document

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(54) **Method of making siloxane compositions**

Herstellungsverfahren von Siloxanzusammensetzungen

Méthode de fabrication de compositions siloxanes

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Description

This invention relates to a method of making siloxane compositions, more specifically compositions wherein high viscosity polysiloxanes are dispersed in volatile, especially cyclic polysiloxanes.

Dispersions of high viscosity polysiloxanes in cyclic polysiloxanes have been known for some time and have been commercially available. These dispersions have a variety of useful characteristics and are important ingredients in many cosmetic compositions. They are generally prepared by physically mixing high viscosity siloxanes into a medium of cyclic siloxanes which have a low viscosity. This method is tedious and requires a lot of energy to ensure a more or less homogeneous dispersion as the high viscosity materials may have a viscosity which amounts to several m²/s. It is possible to dissolve the high viscosity materials in a solvent prior to the dispersion in the cyclic siloxanes in order to reduce the handling viscosity and hence ease the dispersion. However, this leaves the manufacturer with the added disadvantage that a solvent is present and needs to be removed. This disadvantage is all the more serious since the cyclic siloxane materials are volatile to some extent and could be at least partially removed when the solvent is removed.
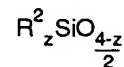
There is a need for a better method of making a dispersion of high viscosity siloxanes in volatile, especially cyclic siloxanes.

We have now found a method of making such dispersion by selectively condensing hydrolisable siloxanes in the presence of volatile, especially cyclic siloxanes using specified catalysts.

According to the invention there is provided a method of making a dispersion of a high viscosity siloxane in a volatile siloxane, said volatile siloxane being a short chain or cyclic siloxane and having a viscosity at room temperature of no more than 10 mm²/s, a boiling point under atmospheric pressure of no more than 250°C and being free from silicon-bonded -OR groups, wherein R denotes a hydrogen atom or an alkyl group having up to 6 carbon atoms which comprises making a first dispersion of organopolysiloxanes having at least 2 silicon-bonded groups -OR in volatile siloxanes, especially cyclic siloxanes of the general formula $(R'_2SiO)_p$, wherein R' denotes hydrogen or an alkyl, alkenyl or aryl group having up to 8 carbon atoms, p denotes an integer with a value of from 3 to 12, followed by contacting said first dispersion with a catalyst which is either (A) a phosphonitrile halide having the general formula $[X(PX_2=N)_nPX_3]^+[MX_{(v-t+1)}R_t]^-$, or (B) a heterogeneous catalyst, selected from lithium hydroxide, magnesium hydroxide, calcium hydroxide, strontium hydroxide, barium hydroxide, sodium borate, sodium phosphate, potassium borate, potassium phosphate, rubidium carbonate, caesium carbonate and carboxylates of rubidium and caesium of the general formula Q.CO.OZ, wherein M is an element having an electronegativity of from 1.0

to 2.0 according to Pauling's scale, Q represents an alkyl group having from 1 to 6 carbon atoms or an alkenyl group having from 2 to 5 carbon atoms, R is an alkyl group having up to 12 carbon atoms, X denotes a halide atom, Z represents Rb or Cs, n has a value of from 1 to 6, v is the valence or oxidation state of M and t has a value of from 0 to (v-1).

Organopolysiloxanes which are suitable for the making of the first dispersion are well known and commercially available materials. They have units of the general formula

$$R^2_z SiO_{\frac{4-z}{2}}$$

wherein R^2 denotes a monovalent hydrocarbon atom having up to 8 carbon atoms and z has a value of from 0 to 3. R^2 may be an alkyl, aryl, aralkyl or alkaryl group. It is, however, preferred that 80% of all R^2 groups are lower alkyl groups or aryl groups, most preferably methyl groups. Most preferably substantially all R^2 groups are methyl groups. It is also preferred that the value of z is 2 for the majority of units, making the organopolysiloxane a polydiorganosiloxane which is a substantially linear polymer. Preferred polymers may have small amounts of units wherein the value of z is 0 or 1, but such units should not amount to more than 5% of the total number of units in the organopolysiloxane. Units where z equals 3 are end-blocking units and no more than 2 of these units will be present unless some branching in the organopolysiloxane has occurred. The organopolysiloxanes must have at least 2 silicon-bonded groups -OR, wherein R denotes a hydrogen atom or an alkyl group having up to 6 carbon atoms. It is preferred that each terminal silicon atom of the organopoly-siloxane has one such silicon-bonded group -OR. Preferred organopolysiloxanes accordingly have the general formula $RO[SiR^2_2O]_mR$, wherein R and R^2 are as defined above, and m is an integer with a value of at least 2. Most preferably R is hydrogen. A suitable example is dimethylsilanol endblocked polydimethylsiloxane. The organopolysiloxanes which are useful for making the first dispersion are preferably linear siloxanes with a viscosity of from 20 to 10,000mm²/s. However, in order to facilitate the mixing process it is preferred to use polymers of slightly lower viscosity, e. g. 20 to 1000mm²/s, more preferably 50 to 500mm²/s and most preferably 60 to 200mm²/s.

Volatile siloxanes are well known and commercially available materials.

Preferred volatile siloxanes are disiloxanes, e.g. hexamethyldisiloxanes. Most preferred are cyclic siloxanes, or mixtures including cyclic siloxanes. It is important that the volatile siloxanes do not have any silicon-bonded groups -OR as defined above, to avoid the polymerisation reaction by condensation of the volatile siloxanes with the organopolysiloxanes having silicon-bonded -OR groups.

Cyclic siloxanes which are useful are also well

known and commercially available materials. They have the general formula $(R'_2SiO)_p$, wherein R' denotes hydrogen or an alkyl, alkenyl or aryl group having up to 8 carbon atoms, $\underline{p}$ denotes an integer with a value of from 3 to 12. Preferably at least 80% of all R' groups are methyl of phenyl groups, most preferably methyl. It is most preferred that substantially all R' groups are methyl groups. Preferably the value of $\underline{p}$ is from 3 to 6, most preferably 4 or 5. Examples of suitable cyclic siloxanes are octamethyl cyclotetrasiloxane, decamethyl pentacyclosiloxane, cyclopenta (methylvinyl) siloxane, cyclotetra (phenylmethyl) siloxane and cyclopenta methylhydrosiloxane. One particularly suitable commercially available material is a mixture of octamethylcyclo-tetrasiloxane and decamethylcyclopentasiloxane.

The first dispersion may be made in any convenient way, preferably by mixing the ingredients mechanically. Standard equipment can be used for this dispersion. Suitable equipment includes ribbon blending, homogenisers etc. The ratio of organopolysiloxanes to volatile or cyclic siloxanes in the first dispersion may vary from 1/100 to 10/1. It is, however, preferred that the ratio is from 1/100 to 1/1, more preferably from 1/20 to 1/2, most preferably 1/10 to 1/4. Higher amounts of volatile siloxanes are particularly preferred, as this allows for the final dispersion to have a viscosity which can easily be handled, even when the high viscosity siloxane has a viscosity of several m^2/s.

Organopolysiloxanes which are used in the formation of the first dispersion may also include endblocking units. These are e.g. organosilicon compounds which have only one silicon-bonded group -OR per molecule, and may be silanes (e.g. trimethylsilanol, vinyldimethylsilanol) or siloxanes (e.g. α-hydroxydimethylsiloxane).

Suitable catalysts for the method of the invention may be any of a number of materials.

Catalysts (A) which are useful in the method of the invention have a cationic phosphonitrile part and an anionic part which has been derived from a Lewis acid. The cationic phosphonitrile part is a linear oligomeric or polymeric phosphonitrile halide having the general formula $[X(PX_2=N)_nPX_3]^+$ wherein $\underline{n}$ denotes an integer having a value of from 1 to 6. It is preferred that the halogen X is a chlorine atom. Phosphonitrile halide cationic parts with a value for $\underline{n}$ which is higher than 6 are less suitable as catalysts. Most preferred are the cationic phosphonitrile halide parts in which the value of $\underline{n}$ is from 2 to 4. It is particularly preferred that the amount of phosphonitrile halide polymer in which $\underline{n}$ has a value of 2 is as high as possible as this gives the most active catalyst. Particularly preferred is a catalyst which exclusively consists of compounds according to the above formula in which the value of $\underline{n}$ is 2.

The anionic part of the catalyst (A) is derived from a Lewis acid and has the formula $[MX_{(v-t+1)}R_t]^-$. Although it is preferred that the value of $\underline{t}$ is zero alkyl groups may be included. Preferably the Lewis acid based anion contains a halide X which is the same as the halide of the

phosphonitrile cationic part, i.e. most preferably a chlorine. The element M of the Lewis acid part is an electropositive element having an electronegativity value according to Pauling's scale of from 1 to 2, preferably from 1.2 to 1.9, most preferably 1.5 to 1.9. Suitable elements are found in Groups Ib, IIa, IIb, IIIa, IVa, IVb, Va, Vb, VIb, VIIb and VIII of the Periodic Table. They include Al, B, Be, Mg, Sb and Si. It is preferred that the difference in electronegative value between the phosphorus atom of the phosphonitrile part of the catalyst and the M element is as large as possible within the preferred range, giving improved catalytic activity when this value is larger. A suitable compound is the one where the Lewis acid derived portion is based on antimony, especially $SbCl_3$ or $SbCl_5$ or aluminium, especially $AlCl_3$. An example of such suitable catalyst (A) has the formula $[Cl_3P=N-(PCl_2=N)_s-PCl_3]^+[SbCl_6]^-$, wherein $\underline{s}$ has a value from 1 to 4.

Phosphonitrile halide catalysts (A) which are useful in the method of the invention have been described fully in application No. G.B. 2 252 969 and may be made by reacting in the presence of an aromatic hydrocarbon or of a chlorinated aliphatic or aromatic hydrocarbon, e.g. toluene, sym-tetrachloroethane or 1,2,4-trichlorobenzene, as inert solvent, a phosphorus pentahalide, e.g. phosphorus pentachloride, an ammonium halide, e.g. ammonium chloride and a selected Lewis acid. The reaction may be carried out at a temperature between 100 and 220°C, followed by separating the reaction products from the solids and the volatile components, thus isolating the liquid reaction product. The reagents may be contacted for a period of time which may vary from 2 to 10 hours. It is preferred to continue the reaction for a period in excess of 6 hours. From 0.1 to 1 mole, preferably 0.3 to 0.6 mole of the selected Lewis acid is provided for each mole of phosphorus pentahalide. The catalyst which is useful in the method of the invention can be conveniently stored in solvent, e.g. CH_2Cl_2 preferably under a blanket of nitrogen.

The phosphonitrile halide catalysts (A) may be used at a concentration of from 1 to 500ppm by weight based on the total weight of the organopolysiloxanes which are to be polymerised. Preferably from 5 to 150ppm by weight are used, most preferably from 5 to 50ppm. The amount of catalyst used in the method of the invention may be reduced when the temperature at which the organosilicon compounds and the catalyst are contacted is increased. The method of the invention may conveniently be carried out at room temperature. The temperature may also be as high as 150°C. Preferably, however, the temperature range is from 10 to 100°C, most preferably from 20 to 50°C. The higher the temperature the more chance that some of the volatile, especially cyclic siloxanes are lost from the reaction mixture due to their lower boiling point. If higher temperatures are used it is preferred to increase the pressure of the reaction to some extent. Catalysts (A) can easily be neutralised at the end of the polymerisation reaction in order to stabi-

lise the reaction product, e.g. in respect of its viscosity. The neutralisation may be done at any stage of the condensation process, e.g. as soon as the desired viscosity of the organopolysiloxanes is reached. Neutralisation agents for the catalysts are alkaline materials, preferably lightly alkaline materials for example primary, secondary and tertiary amines, ammonia, amides, imides and cyclic diamines. Examples of suitable neutralisation agents are diethylamine, propylamine, ammonia, hexamethyldisilazane, piperazine, methylmorpholine and succinamide.

Due to the low amount of catalyst (A) required and the ease of terminating the condensation reaction, Catalyst (A) is particularly useful in both batch and continuous processes. Catalyst (A), though also useful as a rearrangement catalyst for polydiorganosiloxanes, is much more effective as a condensation catalyst. It is, therefore, particularly interesting to use Catalyst (A) in the method of the invention as rearrangement would only occur when the condensation reaction has finished.

A second group of useful catalysts in the method of the invention is concerned with a group of heterogeneous catalysts (B). Because of their heterogeneous nature these catalysts are also particularly adapted for use in processes involving manufacture on a continuous, rather than a batch, basis. Properly employed such so-called "continuous processes" avoid the delays and costs common to batch processing, for example those involved in the charging and discharging of the reaction vessel and separation of the catalyst material from the product. When carrying out the process of this invention in a continuous mode contact between the catalyst material and the organosilicon compound may be achieved by passing the organosilicon compound over or through a bed of the catalyst material. When employing more viscous reactants or products it may be necessary to adjust the porosity of the bed by granulation of the catalyst or other means. We have found that a particularly suitable form of bed for continuous operation can be obtained by depositing the catalyst substance in or on an inert particulate material, for example silica, having a particle size appropriate to the desired porosity of the bed.

A first type of heterogeneous catalyst (B) consists of borates or phosphates of sodium or potassium. Specific examples of such catalysts are $K_2B_4O_7.4H_2O$, $K_2BO_2.xH_2O$, $K_2B_{10}O_{16}.8H_2O$, $K_3PO_4.xH_2O$, $Na_2B_4O_7.4H_2O$, $NaBO_3.4H_2O$, $NaBO_2.xH_2O$ and $Na_3PO_4.12H_2O$. The sodium and potassium compounds may be employed in their anhydrous or hydrated forms. In the case of the phosphate compounds the phosphate anion should not contain hydrogen. Thus, the phosphates of sodium and potassium employed according to this invention do not include the hydrogen phosphates.

A second type of heterogeneous catalyst (B) is any hydroxide of lithium, magnesium, calcium, strontium or barium, the preferred substances being strontium hydroxide and barium hydroxide. The compounds may be employed in their anhydrous or hydrated forms.

A third type of heterogeneous catalyst (B) is a carbonate or carboxylate of rubidium or caesium. In the general formula of the carboxylates Q may be for example methyl, ethyl, propyl, hexyl, vinyl or allyl. Specific examples of catalyst (B) are rubidium carbonate, caesium carbonate, rubidium acetate, caesium propionate, caesium butyrate and rubidium acrylate.

The particle size of the heterogeneous catalyst (B) is not critical. Generally, the smaller the particles the greater the catalytic surface available. However, very fine particle size powders may be more difficult to remove from the condensation product.

In one of its aspects the process of this invention involves contacting the first dispersion with the heterogeneous catalyst (B) at a temperature at which the desired rate of molecular weight increase occurs. The temperatures employed may vary within wide limits for example from about 30°C to about 200°C. Reaction at the lower temperatures is, however, normally too slow for commercial purposes and the process is preferably carried out at temperatures within the range from about 70°C to 150°C. It is also preferred to accelerate the removal of water formed during the condensation reaction by carrying out the process under reduced pressure, that is, at a pressure less than normal atmospheric and most preferably less than about 0.5 bar. One method of carrying out the process is by means of a batch procedure. For example, the catalyst (B) may be codispersed in the first dispersion and this mixture raised to the required temperature. Alternatively, the first dispersion may be preheated prior to the addition of the catalyst (B). Advantageously the mixture is agitated during the reaction period to maintain the catalyst in suspension. Sufficient catalyst (B) is employed to achieve the desired rate of condensation having regard to the nature and geometry of the processing equipment, temperature and other factors. From considerations of speed of reaction and economy of operation we prefer to employ from about 0.001 to about 8% by weight more preferably 0.1 to 5% of the catalyst (B) based on the weight of the organopolysiloxane in the first dispersion.

Termination of the condensation reaction when using catalyst (B) in the method of the invention may be achieved by lowering the temperature of the mixture, and/or raising the reaction pressure to atmospheric and/or by separation or neutralisation of the catalyst.

The final product obtained by the method of the invention is a dispersion of a high viscosity siloxane, having a structure which is dependant on the structure of the organopolysiloxane starting materials used in making the first dispersion. When the preferred organopolysiloxanes are used the final high viscosity siloxanes have the average formula $RO[SiR^2_2O]_mSiR^2_2OR$, wherein R and R^2 are as defined above and $\underline{m}$ has a value which is substantially higher than the number of organosiloxane units present in the organopolysiloxanes used to make the first dispersion. The viscosity

of the high viscosity siloxanes may be as low as 10,000mm²/s or as high as several millions of mm²/s, thus forming a siloxane gum. The final product will have a weight ratio of high viscosity siloxane polymer to cyclic siloxane which is very close to the ratio of organopolysiloxane to cyclic siloxanes of the first dispersion. This is due to the fact that the only change in weight is due to the formation and removal of H_2O molecules or ROH molecules upon condensation or the organopolysiloxanes. Traces of catalyst which may remain in the final dispersion may be removed by known methods, i.e. filtration or evaporation.

There now follow a number of examples which illustrate the invention. All parts, ratios and percentages are by weight unless otherwise stated.

Example 1

0.12 mole of PCl_5, 0.08 mole of NH_4Cl and 0.04 mole of $SbCl_5$ were allowed to react together in 60ml of symtetrachloroethane at its refluxing temperature of 147°C for 3.5 hours. After the reaction the solution was filtered to remove insoluble compounds, followed by removal of the solvent under reduced pressure. A bright yellow liquid was obtained which slowly crystallised upon cooling. The resulting catalyst was analysed by NMR (nuclear magnetic resonance) spectroscopy. It was found to be a 50/50 mixture of $[PCl_3=N-PCl_2=N-PCl_3]^+$ $[SbCl_6]^-$ and $[PCl_3=N-(PCl_2=N)_2-PCl_3]^+[SbCl_6]^-$ while no $[PCl_6]^-$ anion was observed. 50 parts of dimethylsilanol endblocked polydimethylsiloxane were mixed with 50 parts of octamethyltetracyclosiloxane and homogenised into a first dispersion. 48ppm based on the weight of the polydimethylsiloxane of the catalyst as prepared above were added and the mixture allowed to react at 20°C under reduced pressure of 20mm Hg. After 15 minutes the reaction was halted by neutralising the catalyst with 50 ppm of diethylamine. The finished dispersion consisted of 50 parts of a high viscosity siloxane having a viscosity of at least 500,000mm²/s and thus forming a siloxane gum in 50 parts of unchanged octamethyl cyclotetrasiloxane, giving the dispersion an overall viscosity of 12,000mm²/s.

Example 2

13 parts of an α,w-hydroxyl dimethylpolysiloxane having an average structure of $H[OSi(CH_3)_2]_nOH$, wherein n has the average value of 32, were mixed with 83 parts of a mixture of octamethylcyclotetrasiloxane and decamethylpentacyclosiloxane. The mixture was heated to reflux temperature (about 180°C) at atmospheric pressure in the presence of 2% of anhydrous potassium carbonate, based on the weight of the dimethylpolysiloxane. Condensation water was collected in a Dean & Stark apparatus. After 7 hours the reaction was stopped. The catalyst was filtered out and the final product was analysed by gel permeation chromatography.

This analysis showed that the polydimethylsiloxane had condensed to form high viscosity siloxanes with an average molecular weight of 196,464, and that the cyclic siloxanes were unreacted. The final product was a clear dispersion of the high viscosity siloxanes in the cyclic siloxanes.

Example 3

15 parts of an α,w-hydroxyl dimethylpolysiloxane having an average structure of $H[OSi(CH_3)_2]_nOH$, wherein n has the average value of 34, were mixed with 85 parts of a mixture of octamethylcyclotetrasiloxane and decamethylpentacyclosiloxane. The mixture was heated to reflux temperature (about 180°C) at atmospheric pressure in the presence of 0.7% of barium hydroxide octahydrate, based on the weight of the dimethylpolysiloxane. Condensation water was collected in a Dean & Stark apparatus. After 45 minutes the reaction was stopped. The catalyst was filtered out and the final product was analysed by gel permeation chromatography. This analysis showed that the polydimethylsiloxane had condensed to form high viscosity siloxanes with an average molecular weight of 245,000 and that the cyclic siloxanes were unreacted. The final product was a clear dispersion of the high viscosity siloxanes in the cyclic siloxanes.

Example 4

50 parts of an α,w-hydroxyl dimethylpolysiloxane having an average structure of $H[OSi(CH_3)_2]_nOH$, wherein n has the average value of 34, were mixed with 50 parts of a mixture of octamethylcyclotetrasiloxane and decamethylpentacyclosiloxane. The mixture was heated to reflux temperature (about 200°C) at atmospheric pressure in the presence of 5% of strontium hydroxide octahydrate, based on the weight of the dimethylpolysiloxane. Condensation water was collected in a Dean & Stark apparatus. After 2 hours the reaction was stopped. The catalyst was filtered out and the final product was analysed by gel permeation chromatography. This analysis showed that the polydimethylsiloxane had condensed to form high viscosity siloxanes with an average molecular weight of 170,258 and that the cyclic siloxanes were unreacted. The final product was a clear dispersion of the high viscosity siloxanes in the cyclic siloxanes.

Example 5

15 parts of an α,w-hydroxyl dimethylpolysiloxane having an average structure of $H[OSi(CH_3)_2]_nOH$, wherein n has the average value of 34, were mixed with 85 parts of a mixture of octamethylcyclotetrasiloxane and decamethylpentacyclosiloxane. The mixture was heated to reflux temperature (about 130°C) at 260 mm Hg pressure in the presence of 5% of rubidium carbon-

ate, based on the weight of the dimethylpolysiloxane. Condensation water was collected in a Dean & Stark apparatus. After 8 hours the reaction was stopped. The catalyst was filtered out and the final product was analysed by gel permeation chromatography. This analysis showed that the polydimethylsiloxane had condensed to form high viscosity siloxanes with an average molecular weight of 283,796 and that the cyclic siloxanes were unreacted. The final product was a clear dispersion of the high viscosity siloxanes in the cyclic siloxanes.

Example 6

15 parts of an α,w-hydroxyl dimethylpolysiloxane having an average structure of $H[OSi(CH_3)_2]_nOH$, wherein n has the average value of 34, were mixed with 85 parts of a mixture of octamethylcyclotetrasiloxane and decamethylpentacyclosiloxane. The mixture was heated to reflux temperature (about 180°C) at atmospheric pressure in the presence of 5% of tri-sodium orthophosphate dodecahydrate, based on the weight of the dimethylpolysiloxane. Condensation water was collected in a Dean & Stark apparatus. After 8 hours the reaction was stopped. The catalyst was filtered out and the final product was analysed by gel permeation chromatography. This analysis showed that the polydimethylsiloxane had condensed to form high viscosity siloxanes with an average molecular weight of 266,390 and that the cyclic siloxanes were unreacted. The final product was a clear dispersion of the high viscosity siloxanes in the cyclic siloxanes.

Example 7

50 parts of an α,w-hydroxyl dimethylpolysiloxane having an average structure of $H[OSi(CH_3)_2]_nOH$, wherein n has the average value of 34, were mixed with 50 parts of a mixture of octamethylcyclotetrasiloxane and decamethylpentacyclosiloxane. The mixture was heated to reflux temperature (about 100°C) at 75mm Hg pressure in the presence of 5% of sodium metaborate octahydrate, based on the weight of the dimethylpolysiloxane. Condensation water was collected in a Dean & Stark apparatus. After 8 hours the reaction was stopped. The catalyst was filtered out and the final product was analysed by gel permeation chromatography. This analysis showed that the polydimethylsiloxane had condensed to form high viscosity siloxanes with an average molecular weight of 266,390 and that the cyclic siloxanes were unreacted. The final product was a clear dispersion of the high viscosity siloxanes in the cyclic siloxanes.

Examples 8 - 11

x parts of an α,w-hydroxyl dimethylpolysiloxane having an average structure of $H[OSi(CH_3)_2]_nOH$, wherein n has the average value of 34, were mixed with

y parts of a mixture of octamethylcyclotetrasiloxane and decamethylpentacyclosiloxane. The mixture was heated to reflux temperature (about 130°C) at 300mm Hg pressure in the presence of 5% of lithium hydroxide monohydrate, based on the weight of the dimethylpolysiloxane. Condensation water was collected in a Dean & Stark apparatus. After 2 hours the reaction was stopped. The catalyst was filtered out and the final product was analysed by gel permeation chromatography. This analysis showed that the polydimethylsiloxane had condensed to form high viscosity siloxanes with an average molecular weight of z and that the cyclic siloxanes were unreacted. The final product was a clear dispersion of the high viscosity siloxanes in the cyclic siloxanes. The values of x, y and z are given in the table below.

Example	x	y	z
8	15	85	80,000
9	35	65	145,000
10	50	50	245,000
11	75	25	349,000

Claims

1. A method of making a dispersion of a high viscosity siloxane in a volatile siloxane, said volatile siloxane being a short chain or cyclic siloxane and having a viscosity at room temperature of no more than 10 mm²/s, a boiling point under atmospheric pressure of no more than 250°C and being free from silicon-bonded -OR groups, wherein R denotes a hydrogen atom or an alkyl group having up to 6 carbon atoms which comprises making a first dispersion of organopolysiloxanes having at least 2 silicon-bonded groups -OR, in a volatile siloxane, followed by contacting said first dispersion with a catalyst which is either (A) a phosphonitrile halide having the general formula $[X(PX_2=N)_nPX_3]^+[MX_{(v-t+1)}R_t]^-$, or (B) a heterogeneous catalyst, selected from lithium hydroxide, magnesium hydroxide, calcium hydroxide, strontium hydroxide, barium hydroxide, sodium borate, sodium phosphate, potassium borate, potassium phosphate, rubidium carbonate, caesium carbonate and carboxylates of rubidium or caesium of the general formula Q.CO.OZ, wherein M is an element having an electronegativity of from 1.0 to 2.0 according to Pauling's scale, Q represents an alkyl group having from 1 to 6 carbon atoms or an alkenyl group having from 2 to 5 carbon atoms, R is an alkyl group having up to 12 carbon atoms, X denotes a halide atom, Z represents Cs or Rb, n has a value of from 1 to 6, v is the valence or oxidation state of M and t has a value of from 0 to (v-1).

2. A method according to Claim 1, wherein the volatile

siloxane is a cyclic siloxane of the general formula $(R'_2SiO)_p$ wherein R' denotes hydrogen or an alkyl, alkenyl or aryl group having up to 8 carbon atoms, p is an integer with a value of from 3 to 12.

3. A method according to Claim 1 or 2, wherein substantially all groups R' and R^2 are methyl groups.

4. A method according to any one of the preceding claims, wherein the organopolysiloxane is a substantially linear siloxane polymer, having on each terminal siloxane unit a silicon-bonded group OH.

5. A method according to any one of the preceding claims, wherein the viscosity of the organopolysiloxane used is from 50 to 500mm²/s.

6. A method according to any one of the preceding claims, wherein the weight ratio of organopolysiloxane to volatile siloxane used in the first dispersion is from 1/20 to 1/2.

7. A method according to any one of the preceding claims, wherein the catalyst is neutralised when the high viscosity siloxane has reached the desired viscosity.

8. A method according to any one of the preceding claims, wherein catalyst (A) is used in an amount of from 5 to 50ppm by weight based on the weight of the organopolysiloxane.

9. A method according to any one of the preceding claims wherein M denotes Sb and n has a value of 2.

10. A method according to any one of Claims 1 to 7, wherein catalyst (B) is used in the form of a catalyst bed in an amount of from 0.1-5% by weight based on the weight of the organopolysiloxane.

Patentansprüche

1. Verfahren zur Herstellung einer Dispersion eines hochviskosen Siloxans in einem flüchtigen Siloxan, wobei das flüchtige Siloxan ein kurzkettiges oder cyclisches Siloxan ist und eine Viskosität bei Raumtemperatur von nicht mehr als 10 mm²/s hat, einen Siedepunkt bei atmosphärischem Druck von nicht mehr als 250°C hat und frei von siliciumgebundenen Gruppen -OR ist, wobei R ein Wasserstoffatom oder eine Alkylgruppe mit bis zu 6 Kohlenstoffatomen bedeutet, das umfaßt, daß man eine erste Dispersion von Organopolysiloxanen mit mindestens zwei siliciumgebundenen Gruppen -OR in einem flüchtigen Siloxan herstellt und anschließend die erste Dispersion mit einem Katalysator in Kontakt bringt, der entweder (A) ein Phosphonitrilhalogenid

mit der allgemeinen Formel $[X(PX_2=N)_nPX_3]^+$ $[MX_{(v-t+1)}R_t]^-$ oder (B) ein heterogener Katalysator ist, ausgewählt aus Lithiumhydroxid, Magnesiumhydroxid, Calciumhydroxid, Strontiumhydroxid, Bariumhydroxid, Natriumborat, Natriumphosphat, Kaliumborat, Kaliumphosphat, Rubidiumcarbonat, Caesiumcarbonat und Carboxylaten von Rubidium oder Caesium der allgemeinen Formel Q.CO.OZ, worin M ein Element mit einer Elektronegativität von 1,0 bis 2,0 nach der Pauling-Skala ist, Q eine Alkylgruppe mit 1 bis 6 Kohlenstoffatomen oder eine Alkenylgruppe mit 2 bis 5 Kohlenstoffatomen bedeutet, R eine Alkylgruppe mit bis zu 12 Kohlenstoffatomen ist, X ein Halogenidatom bedeutet, Z Cs oder Rb bedeutet, n einen Wert von 1 bis 6 hat, v die Valenz oder der Oxidationszustand von M ist und t einen Wert von 0 bis (v-1) hat.

2. Verfahren nach Anspruch 1, worin das flüchtige Siloxan ein cyclisches Siloxan der allgemeinen Formel $(R'_2SiO)_p$ ist, worin R' Wasserstoff oder eine Alkyl-, Alkenyl- oder Arylgruppe mit bis zu 8 Kohlenstoffatomen bedeutet, p eine ganze Zahl mit einem Wert von 3 bis 12 ist.

3. Verfahren nach Anspruch 1 oder 2, worin im wesentlichen alle Gruppen R' und R^2 Methylgruppen sind.

4. Verfahren nach einem der vorhergehenden Ansprüche, worin das Organopolysiloxan ein im wesentlichen lineares Siloxanpolymer ist, das an jeder endständigen Siloxaneinheit eine siliciumgebundene Gruppe OH aufweist.

5. Verfahren nach einem der vorhergehenden Ansprüche, worin die Viskosität des verwendeten Organopolysiloxans 50 bis 500 mm²/s ist.

6. Verfahren nach einem der vorhergehenden Ansprüche, worin das Gewichtsverhältnis von Organopolysiloxan zu flüchtigem Siloxan, das in der ersten Dispersion verwendet wird, 1:20 bis 1:2 ist.

7. Verfahren nach einem der vorhergehenden Ansprüche, worin der Katalysator neutralisiert wird, wenn das hochviskose Siloxan die gewünschte Viskosität erreicht hat.

8. Verfahren nach einem der vorhergehenden Ansprüche, worin Katalysator (A) in einer Menge von 5 bis 50 ppm (Gewicht), bezogen auf das Gewicht des Organopolysiloxans, verwendet wird.

9. Verfahren nach einem der vorhergehenden Ansprüche, worin M Sb bedeutet und m einen Wert von 2 hat.

10. Verfahren nach einem der Ansprüche 1 bis 7, worin Katalysator (B) verwendet wird in Form eines Kata-lystorbettes in einer Menge von 0,1 bis 5 Gew.-%, bezogen auf das Gewicht des Organopolysiloxans.

Revendications

1. Procédé de préparation d'une dispersion d'un siloxane de haute viscosité dans un siloxane volatil, ledit siloxane volatil étant un siloxane à chaîne courte ou cyclique et ayant une viscosité à température ambiante non supérieure à 10 mm²/s, un point d'ébullition sous pression atmosphérique non supérieur à 250 °C et étant exempt de groupes -OR liés au silicium, où R représente un atome d'hydrogène ou un groupe alkyle ayant jusqu'à 6 atomes de carbone, qui comprend la préparation d'une première dispersion d'organopolysiloxanes ayant au moins 2 groupes -OR liés au silicium, dans un siloxane volatil, puis la mise en contact de ladite première dispersion avec un catalyseur qui est (A) un halogé-nure de phosphonitrile ayant la formule générale [X(PX$_2$=N)$_n$PX$_3$]$^+$[MX$_{(v-t+1)}$R$_t$]$^-$, ou (B) un catalyseur hétérogène choisi parmi l'hydroxyde de lithium, l'hy-droxyde de magnésium, l'hydroxyde de calcium, l'hydroxyde de strontium, l'hydroxyde de baryum, le borate de sodium, le phosphate de sodium, le bo-rate de potassium, le phosphate de potassium, le carbonate de rubidium, le carbonate de césium et les carboxylates de rubidium ou de césium de la for-mule générale Q.CO.OZ, où M est un élément ayant une électronégativité de 1 à 2 d'après l'échel-le de Pauling, Q représente un groupe alkyle ayant de 1 à 6 atomes de carbone ou un groupe alcényle ayant de 2 à 5 atomes de carbone, R est un groupe alkyle ayant jusqu'à 12 atomes de carbone, X re-présente un atome d'halogène, Z représente Cs ou Rb, $\underline{n}$ a une valeur de 1 à 6, $\underline{v}$ est la valence ou l'état d'oxydation de M et $\underline{t}$ a une valeur de 0 à ($\underline{v}$-1).

2. Procédé selon la revendication 1, dans lequel le si-loxane volatil est un siloxane cyclique de la formule générale (R'$_2$SiO)$_p$ où R' représente un hydrogène ou un groupe alkyle, alcényle ou aryle ayant jusqu'à 8 atomes de carbone, $\underline{p}$ est un nombre entier ayant une valeur de 3 à 12.

3. Procédé selon la revendication 1 ou 2, dans lequel substantiellement tous les groupes R' et R² sont des groupes méthyle.

4. Procédé selon l'une quelconque des revendications précédentes, dans lequel l'organopolysiloxane est un polymère de siloxanes substantiellement linéai-re, ayant sur chaque unité siloxane terminale un groupe OH lié au silicium.

5. Procédé selon l'une quelconque des revendications précédentes, dans lequel la viscosité de l'organo-polysiloxane utilisé est de 50 à 500 mm²/s.

6. Procédé selon l'une quelconque des revendications précédentes, dans lequel le rapport pondéral de l'organopolysiloxane au siloxane volatil utilisé dans la première dispersion est de 1/20 à 1/2.

7. Procédé selon l'une quelconque des revendications précédentes, dans lequel on neutralise le cataly-seur lorsque le siloxane de haute viscosité a atteint la viscosité souhaitée.

8. Procédé selon l'une quelconque des revendications précédentes, dans lequel le catalyseur (A) est utili-sé en une quantité de 5 à 50 ppm en poids sur la base du poids de l'organopolysiloxane.

9. Procédé selon l'une quelconque des revendications précédentes, dans lequel M représente Sb et $\underline{n}$ a une valeur de 2.

10. Procédé selon l'une quelconque des revendications 1 à 7, dans lequel le catalyseur (B) est utilisé sous la forme d'un lit de catalyseur, en une quantité de 0,1 à 5 % en poids sur la base du poids de l'orga-nopolysiloxane.